CATHODE MATERIALS FOR NEXT GENERATION LITHIUM-ION BATTERIES: DIAGNOSTIC TESTING AND EVALUATION OF LOW-COBALT CATHODES

Project ID: BAT252

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2021 DOE Vehicle Technologies Office
Annual Merit Review

Overview

Timeline

- Start: October 1, 2018
- End: September 30, 2021
- Percent complete: 85%

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost
  - Performance
  - Safety
  - Cobalt content

Budget

- Total project funding:

  FY20 $4.0M
- ANL, NREL, ORNL, LBNL, PNNL

Partners

- ANL, NREL, ORNL, LBNL, PNNL

Students supported from:

- University of Illinois at Chicago
- University of Rochester
- Oregon State University

Relevance

There is an urgent need to lower the cobalt content of transition-metal-based layered-oxides being considered for high-energy lithium-ion batteries in vehicular applications

- Lithiated layered oxides containing nickel, cobalt, and manganese, such as $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$, are intercalation compounds used as positive electrodes in high-energy lithium-ion batteries
- To improve sustainability, lower cost, and minimize reliance on security critical materials, it is crucial to lower the cobalt content of the these layered oxides
- Our main objective is to develop layered oxides with little or no cobalt, while maintaining the high energy densities, performance, and safety characteristics of the higher-cobalt oxides
- Another objective is to identify mechanisms associated with the performance loss (capacity fade, impedance rise) that occurs during extended cycling and to develop cell chemistries that provide a pathway to achieving cobalt-free cathodes

Approach

See BAT030, BAT167, BAT251 & BAT253

Multi-institutional effort to identify and solve performance loss problems of full cells with low-Co layered-oxide cathodes

Oxide Development

- Precursor Synthesis (MERF, CSE)
- Calcination Optimization: Time, Temperature → Half-cell performance validation
- Oxide Scale-up, Characterization (SEM, XRD DSC, PSA)

Full-cell Tests

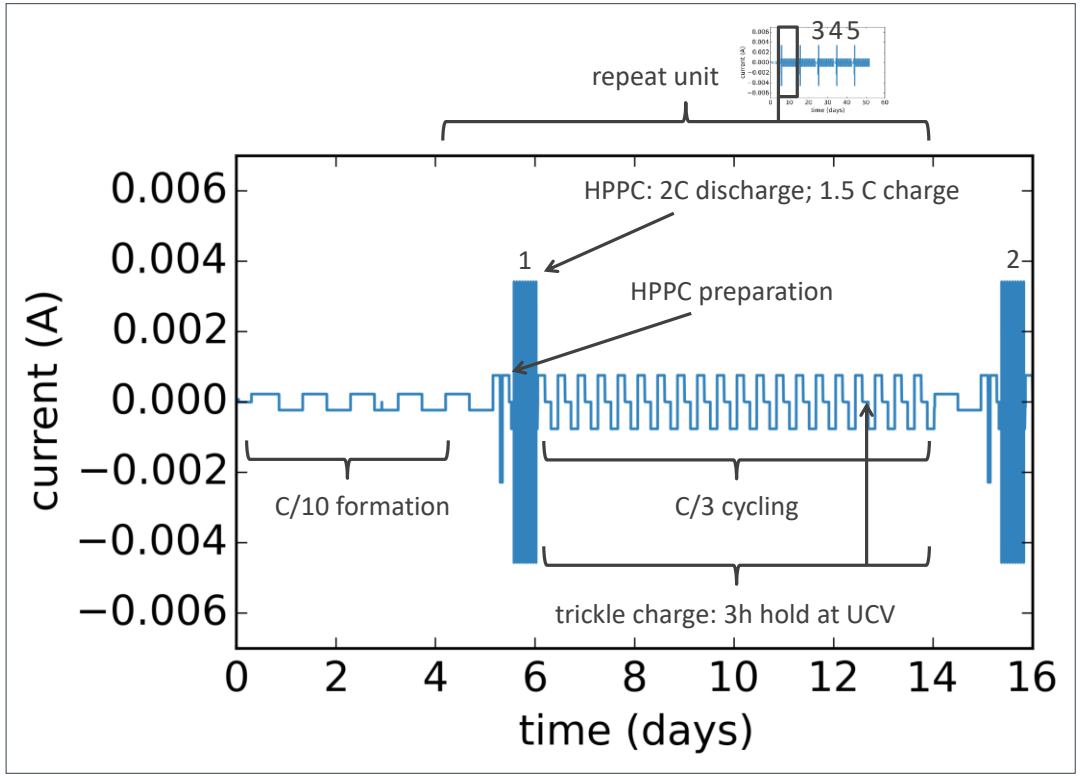
- Electrode coating (CAMP) Distribution to team participants
- Electrochemical testing (coin, 3-electrode, pouch) Gassing analysis
- Electrochemical evaluation of oxide coatings and electrolyte additives

Post-test Characterization

- Cathode study by EChem, SEM, XRD, XPS, TEM (Oxide structure changes, surface reaction products)
- Anode study by EChem, SEM, XRD, XPS, Raman (Graphite structure and SEI changes)
- Separator/Electrolyte study by HPLC, GC-MS, SEM (Pore clogging, electrolyte degradation, TM dissolution)

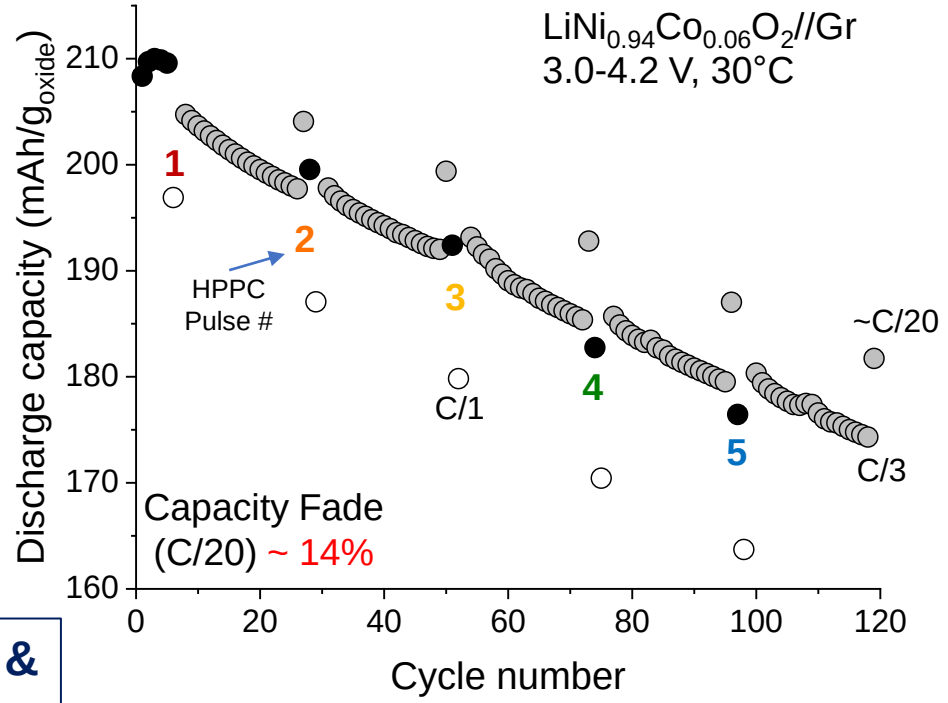
Standard cycling protocols used for full cell tests

Protocol includes 3h hold at 4.2 V to accelerate aging

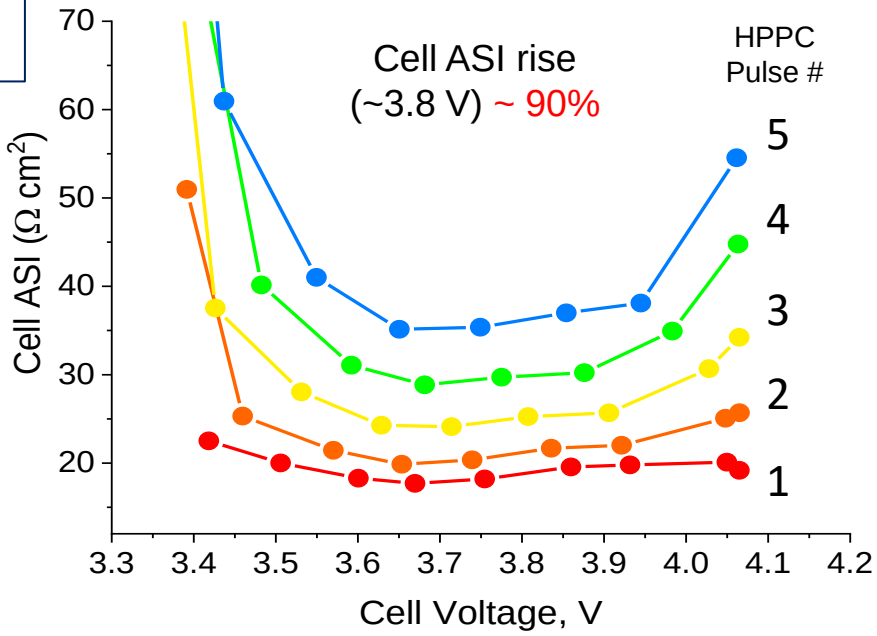


Protocol provides information on cell capacity and impedance changes

Long et al., J. Electrochem. Soc. 163 (2016) A2999



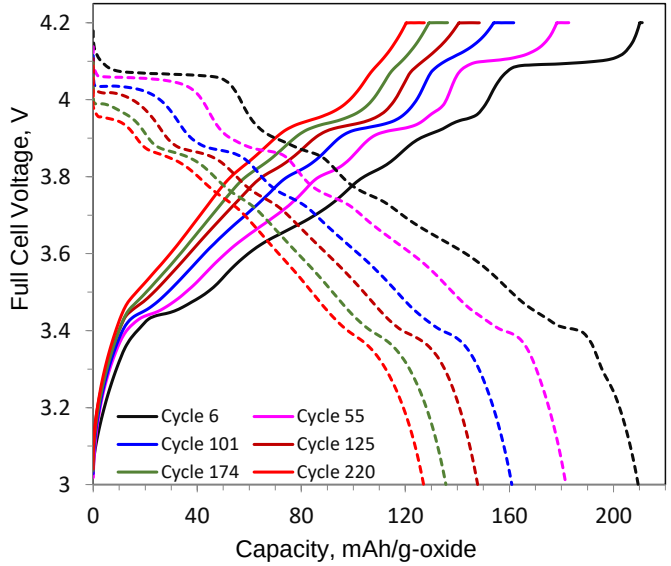
Capacity fade & Impedance rise during cycling

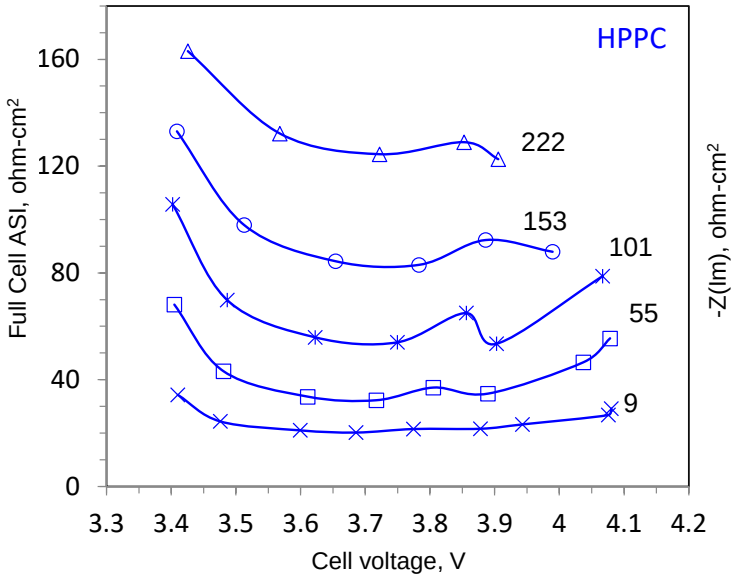


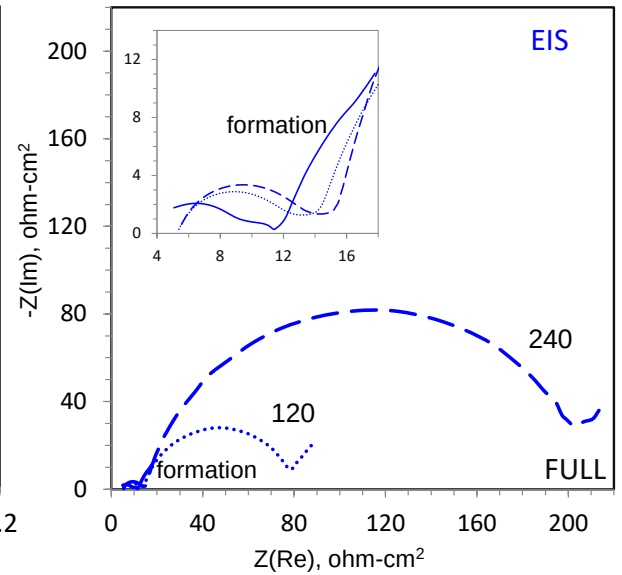
See BAT476

See BAT251

$LiNiO_2$//Gr reference electrode cell: 3.0-4.2 V, 30°C, ~240 cycles

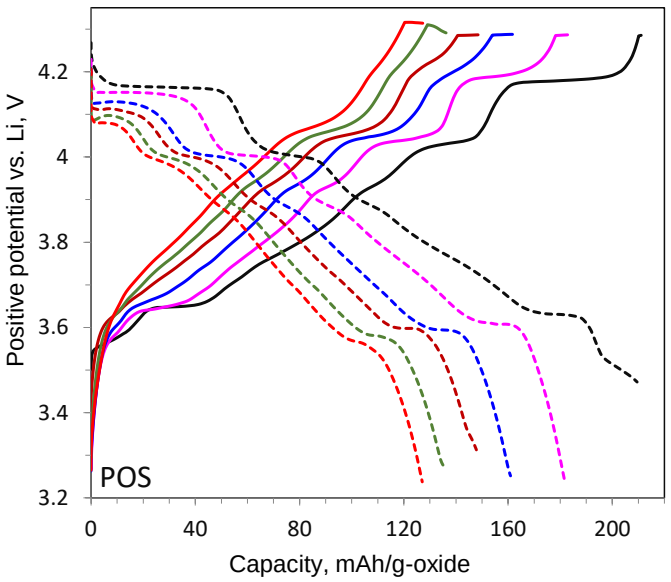


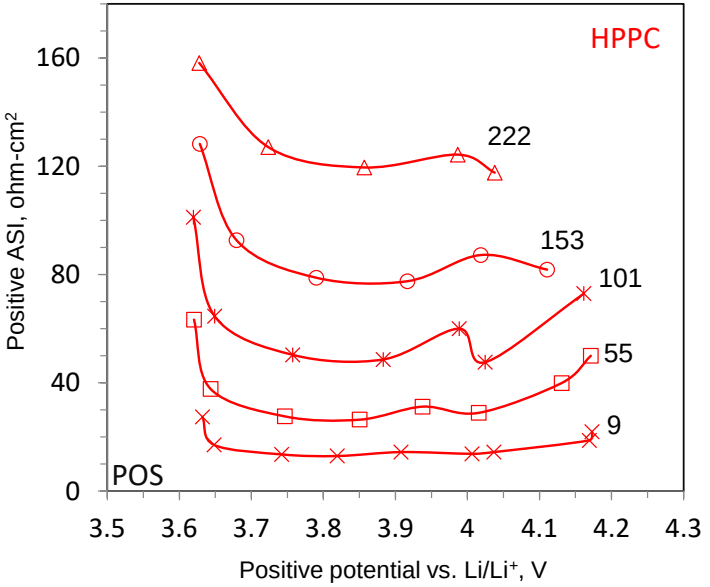


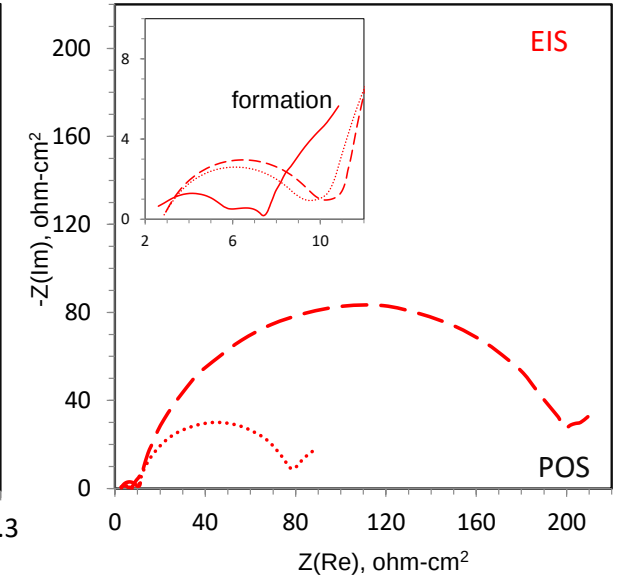


Full cell data show capacity loss and impedance increase during cycling

HPPC & EIS plots show the cycle# at which data were obtained



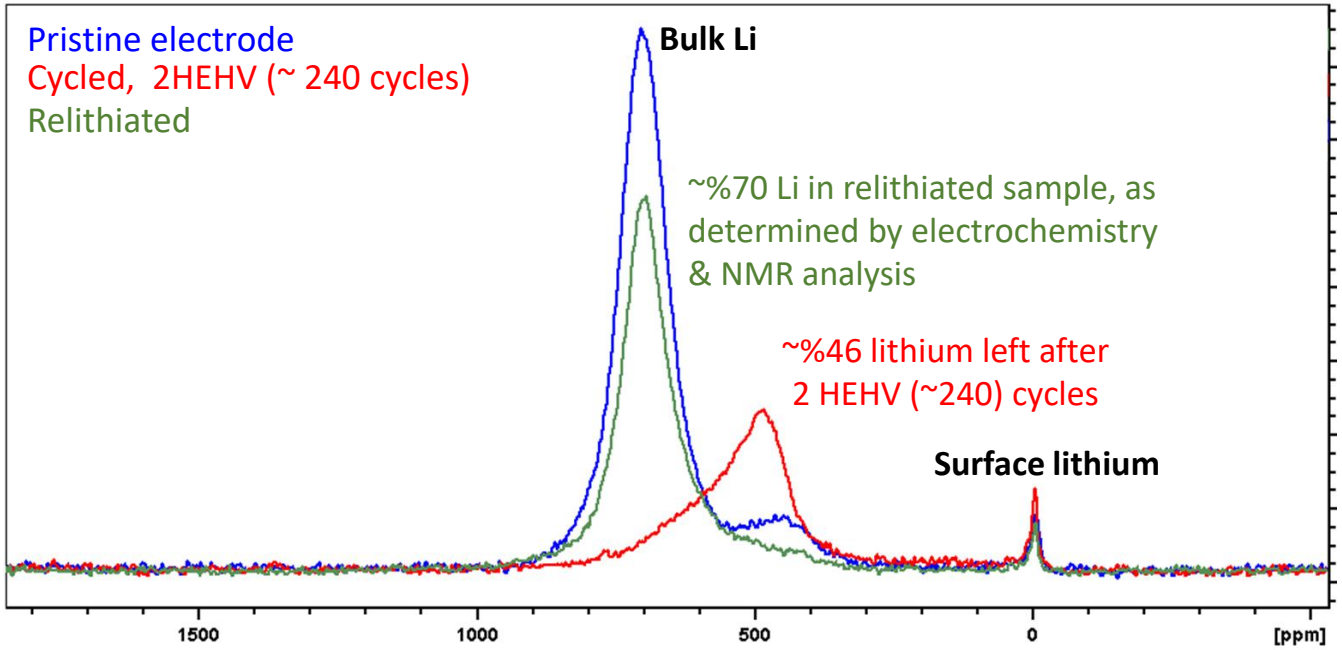


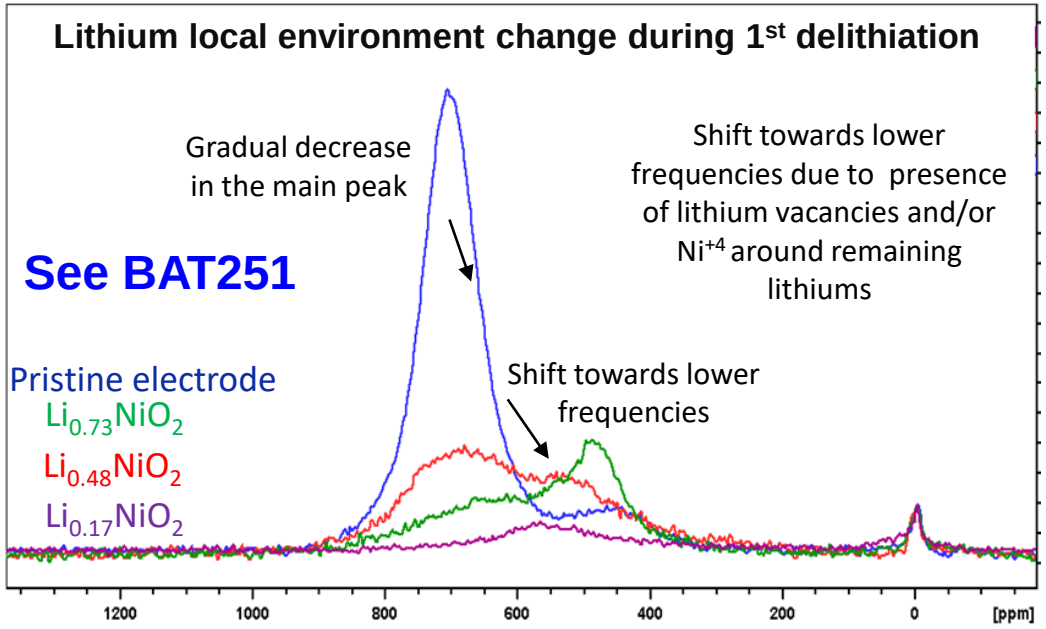


Electrode data show that the positive is the sole contributor to the impedance increase. Capacity loss is mainly from Li trapping in the graphite-SEI. Structural changes in the oxide also contributes to the cell capacity fade.

Structural characterization of cycled $LiNiO_2$ by ^6Li NMR

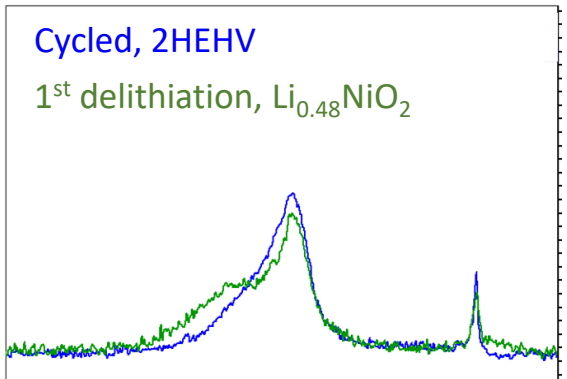
Data indicate structural changes in the oxide during the cycling

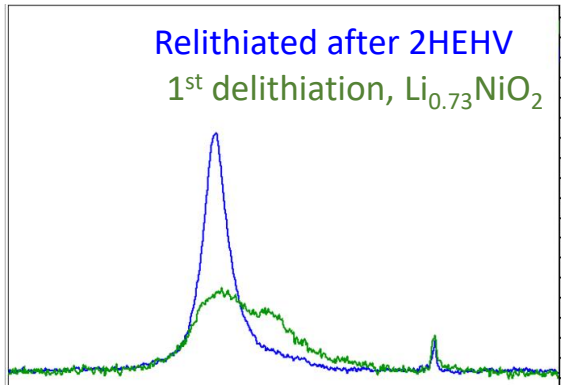




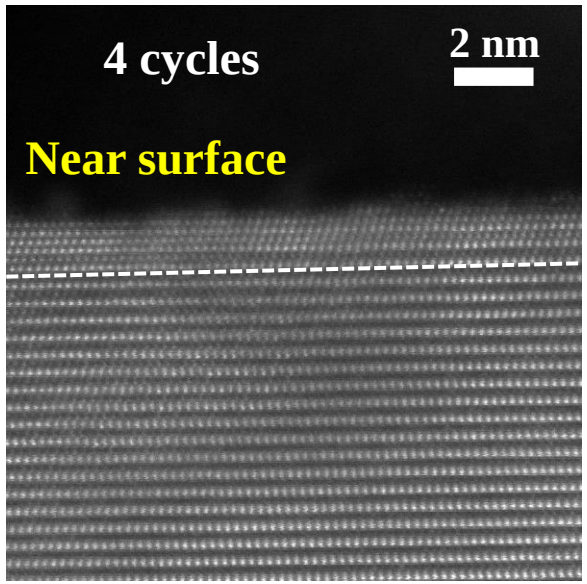
- On extended cycling, original lithium peak completely shifts to lower frequencies due to lithium loss. The local Li environments are very different from those in the pristine oxide. The broad peak suggests Li^+/vacancy and Ni^{3+}/Ni^{4+} coordinations, with additional contributions from under-coordinated Li^+ ions.
- The aged sample was electrochemically-relithiated in a Li-metal cell. On relithiation the Li environments and local order are restored, even though the oxide is 30% deficient in Li^+ ions. The data indicate that 70% of the oxide resembles the pristine material, whereas 30% of the oxide has no Li environments.

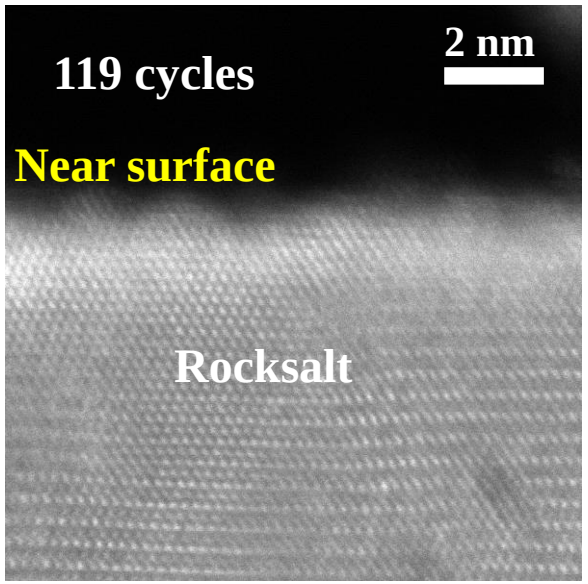
Similar lithium content but different lithium local environments for aged and delithiated samples during 1st charge

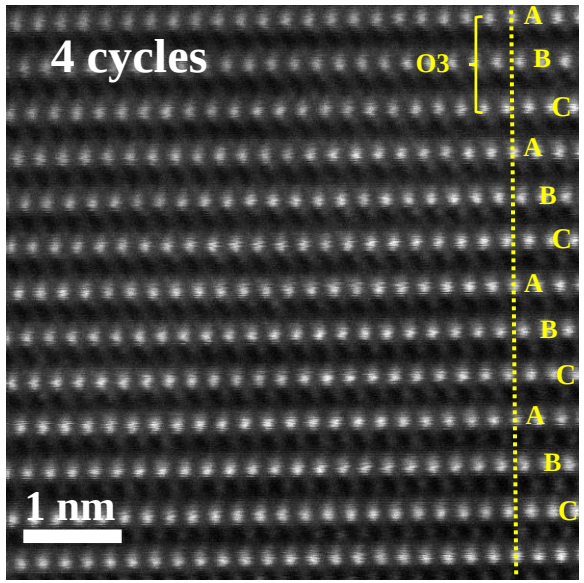


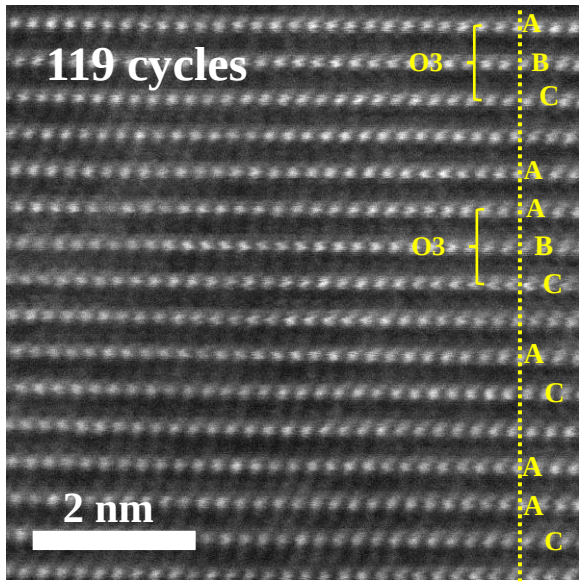


STEM observations of structural changes in cycled $LiNiO_2$









Images near the particle edge

- The pristine oxide particle has a ~1 nm thick rock-salt-like layer near the edges
- Thickness of this layer increases with cycling. After 119 cycles, penetration of this layer into the particle bulk is evident.
- These disordered (non-layered) regions can impede Li+ extraction and insertion during electrochemical cycling

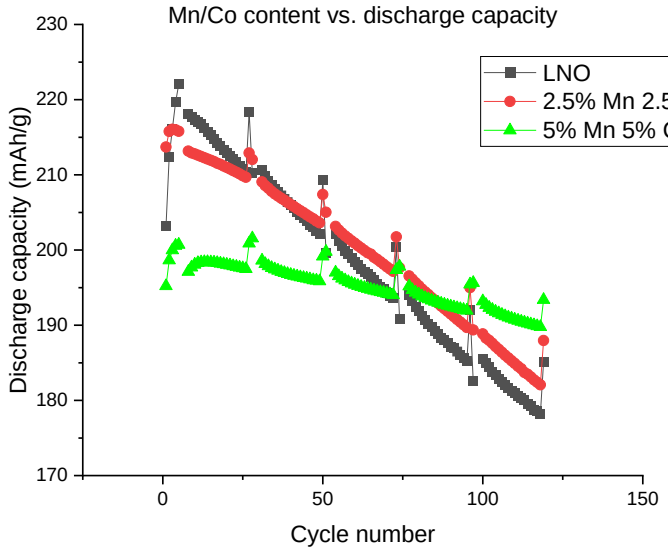
Images of the particle bulk

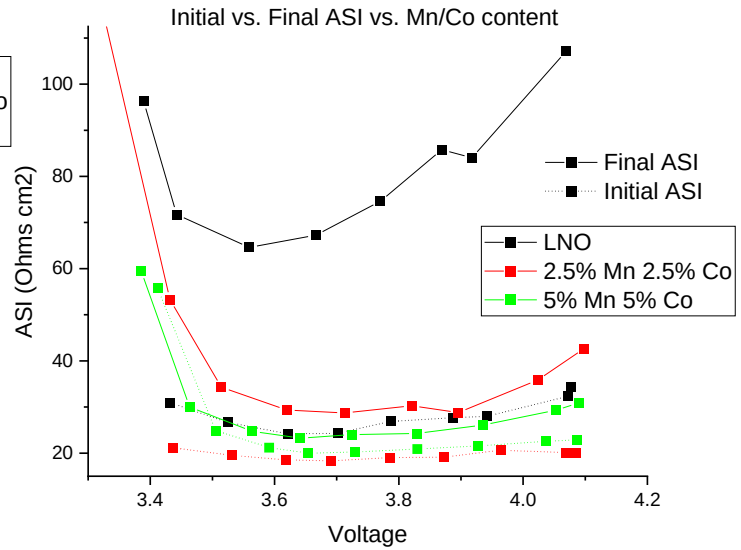
- The pristine oxide lattice has the O3 structure
- During the early cycles, the bulk lattice maintains the O3 structure.
- On extended cycling (119 cycles), the stacking sequences in portions of the oxide are completely disrupted. These portions have significant amounts of Ni in the Li-layers, i.e., Li-deficient regions are formed during the cycling.

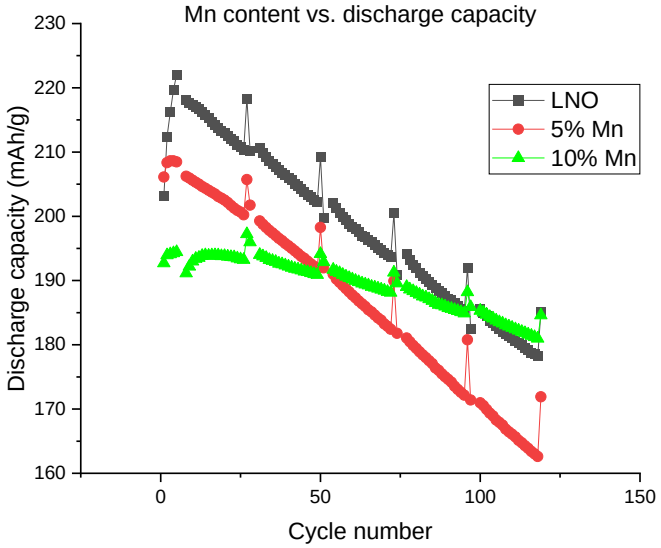
See BAT251

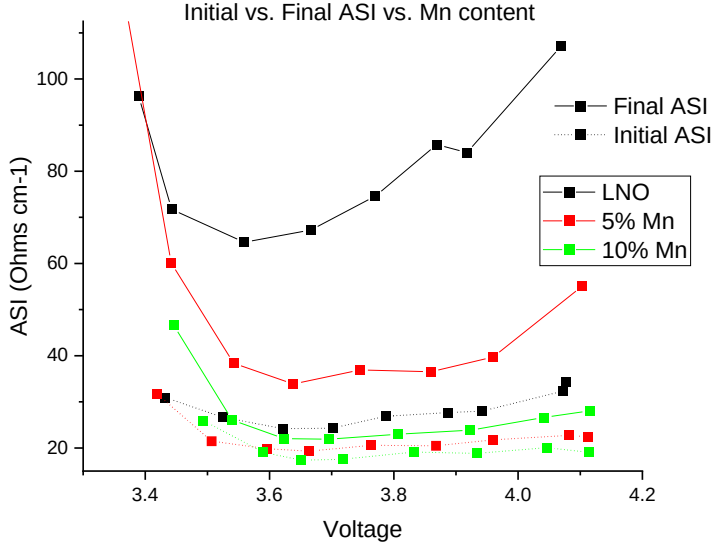
Effect of 5% and 10% dopant on $LiNiO_2$ full-cell performance

Mn and Co *together* improve capacity retention and impedance rise, Mn alone is not as effective







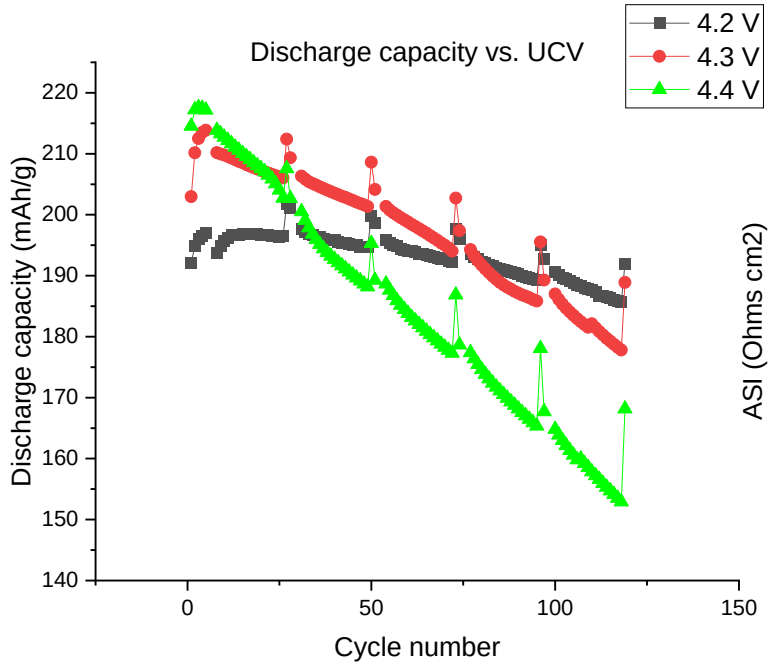


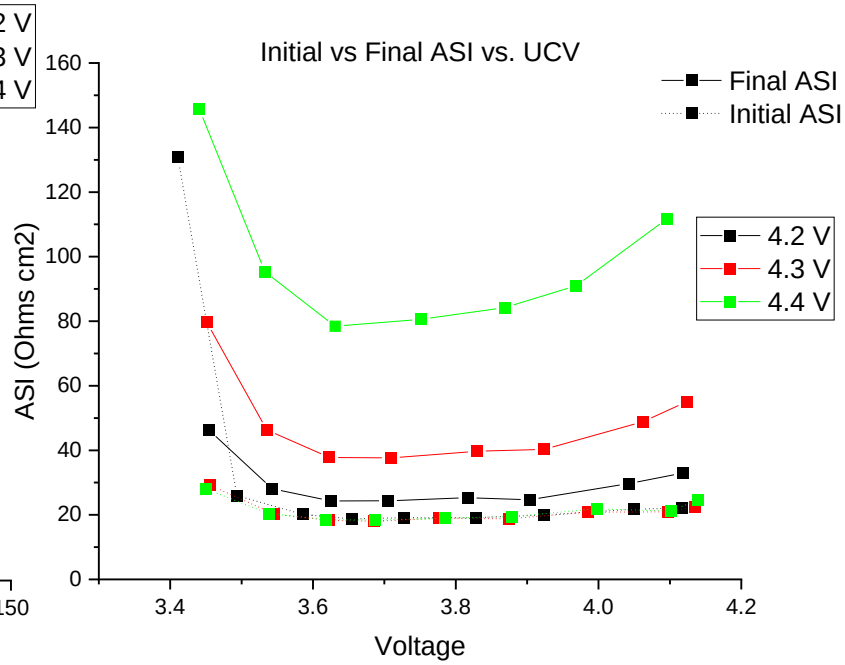
In the 3-4.2 V cycling window

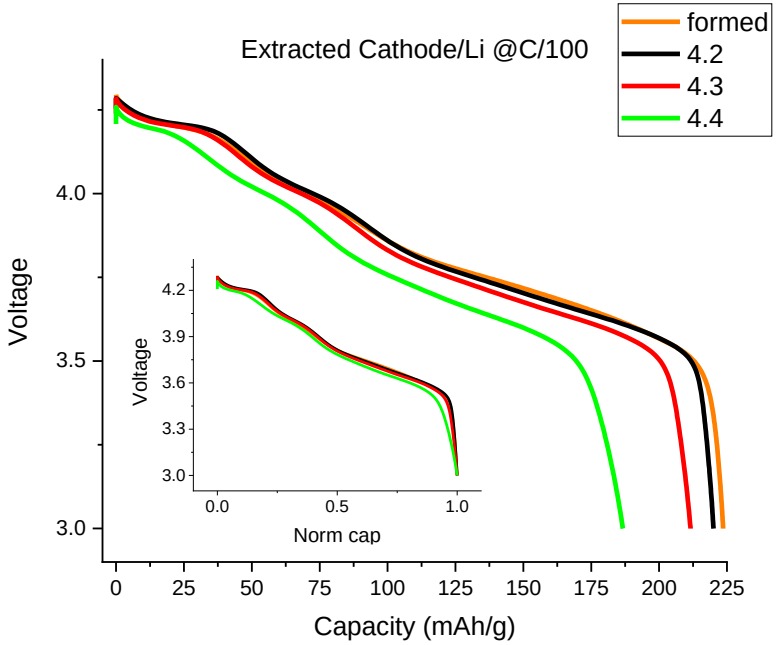
- Adding small amounts of Co and Mn to $LiNiO_2$ lowers initial capacity
- 10% dopant improves capacity retention and decreases impedance rise
- Mn and Co together show capacity retention benefits at 5% and 10% levels whereas Mn alone only shows benefit at 10%.
- 5% dopant lowers impedance rise, with Mn and Co together showing lower impedance rise than Mn alone

Effect of UCV on $LiNi_{0.9}Mn_{0.1}O_2$ full-cell performance

Reactivity increases at higher UCV; some oxide structure changes likely at UCV = 4.4 V







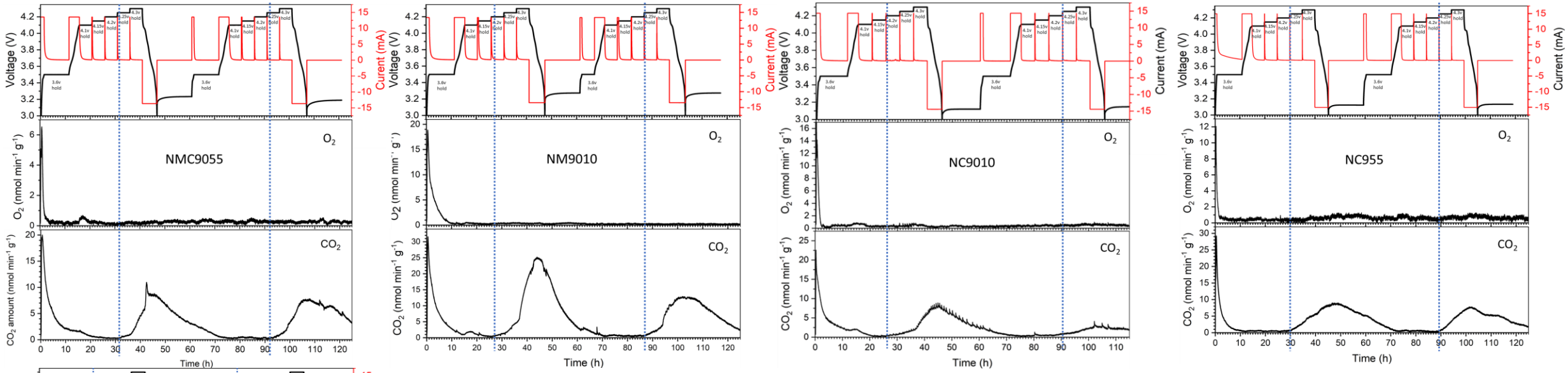
- $LiNi_{0.9}Mn_{0.1}O_2$ shows higher initial capacity at 4.3 V and 4.4 V UCV. However, higher UCVs correspond to a faster capacity loss and lower CE throughout the protocol.
- Impedance rise is significantly affected by UCV, but harvested cathodes after a full HEHV protocol show similar capacities to pristine.
- Extracted cathodes cycled against Li at slow rates show capacity losses that increase with UCV; the normalized capacity voltage profiles indicate small crystallographic structure changes, which could be at the oxide surface or bulk.
- Impedance appears to be the reason for performance loss of $LiNi_{0.9}Mn_{0.1}O_2$ cycled at higher UCVs

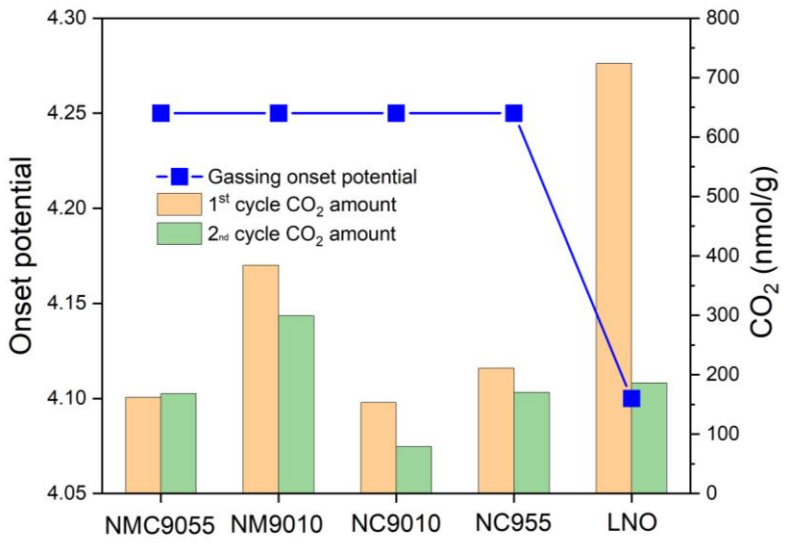
High UCV leads to impedance issues with $LiNi_{0.9}Mn_{0.1}O_2$, but crystal structure is intact after cycling

Gas Analysis on LNO-based Cathodes

LNO = $LiNiO_2$; NM9010 =$LiNi_{0.90}Mn_{0.10}O_2$
NC9010 = $LiNi_{0.90}Co_{0.10}O_2$; NC95=$LiNi_{0.95}Co_{0.05}O_2$
NMC9055 = $LiNi_{0.90}Mn_{0.05}Co_{0.05}O_2$

Gas Generation Onset Potential and Amount Measured by DEMS using Full Cell



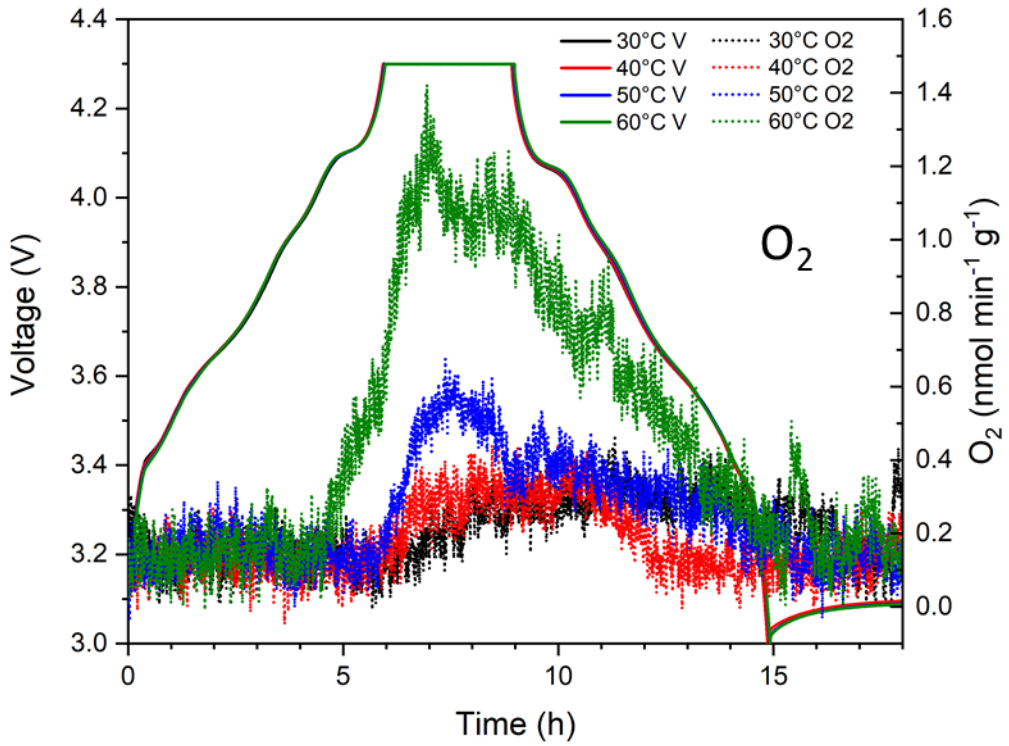


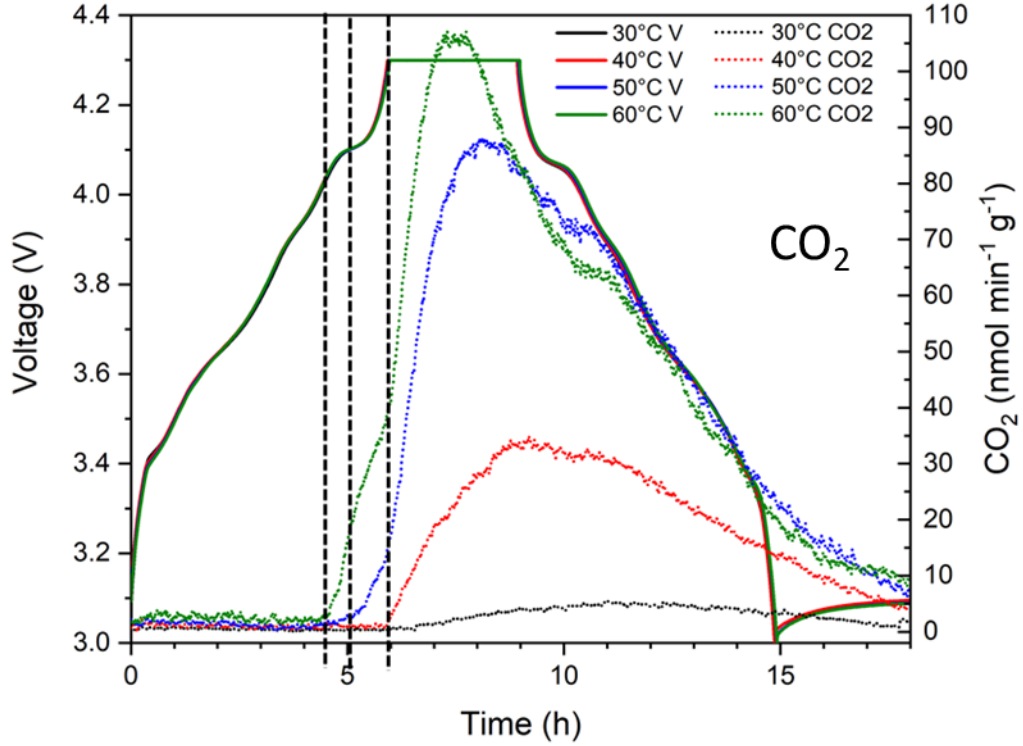
- Higher Ni content LNO-based materials have lower onset potential and generate larger amounts of gases.
- O_2 generation is usually not detected for LNO-based cathodes at high voltages, as it apparently reacts with the electrolyte generating CO_2.
- LNO has a low gassing onset potential of 4.1 V.

NMC9055 = $LiNi_{0.90}Mn_{0.05}Co_{0.05}O_2$

Gassing of NMC9055 at Various Temperatures

Temperature Greatly Impacts Gas Onset Potential and Amounts





	O_2 (nmol)	CO_2(nmol)
30 °C	227	2493
40 °C	213	14902
50 °C	273	35531
60 °C	515	39529

- NMC9055/Graphite single layer pouch cell was used.
- Amounts of gases increase as temperature increases.
- Onset potential for gassing decreases as temperature increases: 4.3V for 30 °C and 40 °C; ~4.1V for 50 °C ; ~4V for 60 °C.

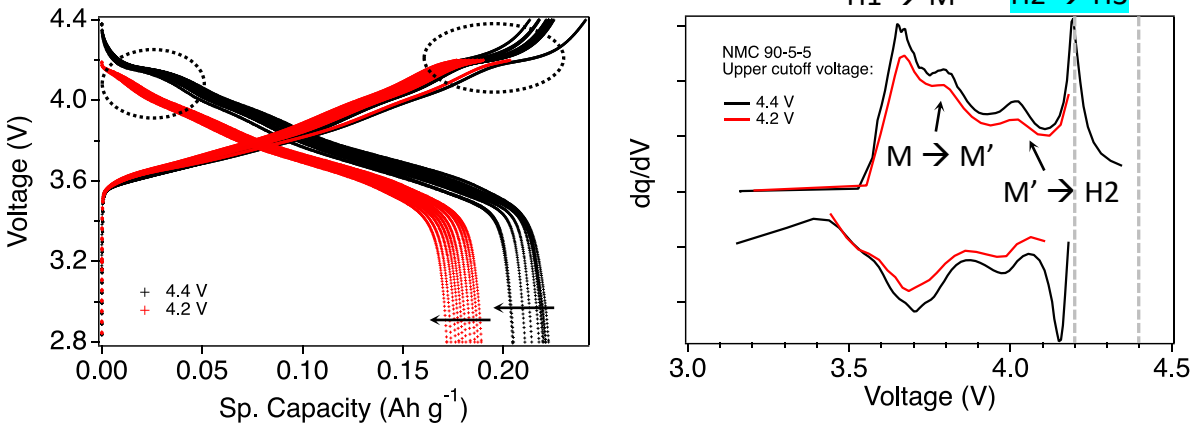
NMC9055 = $LiNi_{0.90}Mn_{0.05}Co_{0.05}O_2$

In Situ Spectroscopic Analysis of NMC9055 with Varying UCVs

Transition Metal Redox, Cathode-Electrolyte Interphase Evolution, and Electrolyte Solution Structure

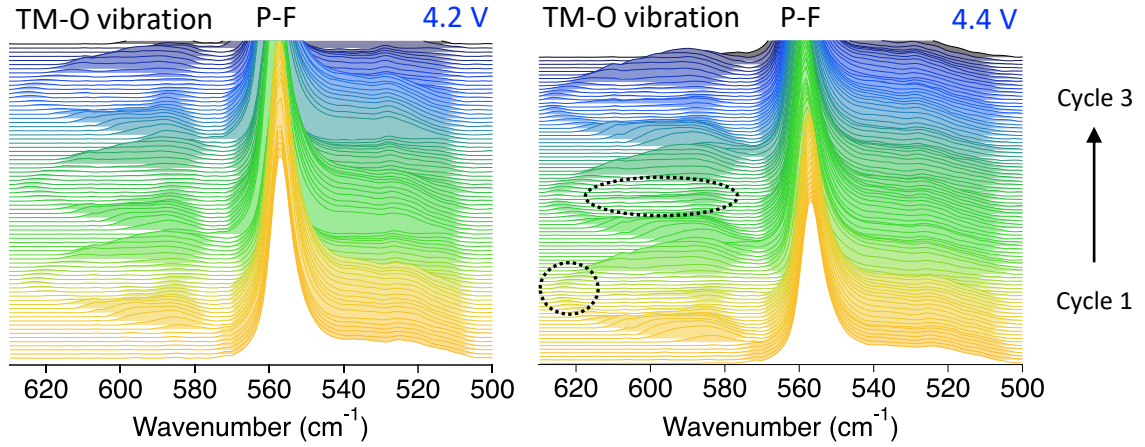
Electrochemical Testing

- 2.8 - 4.2/4.4 V (*vs* Li/Li^+); C/10 for 10 cycles (1C = 200 mAh/g)
- Reliable electrochemical performance obtained.



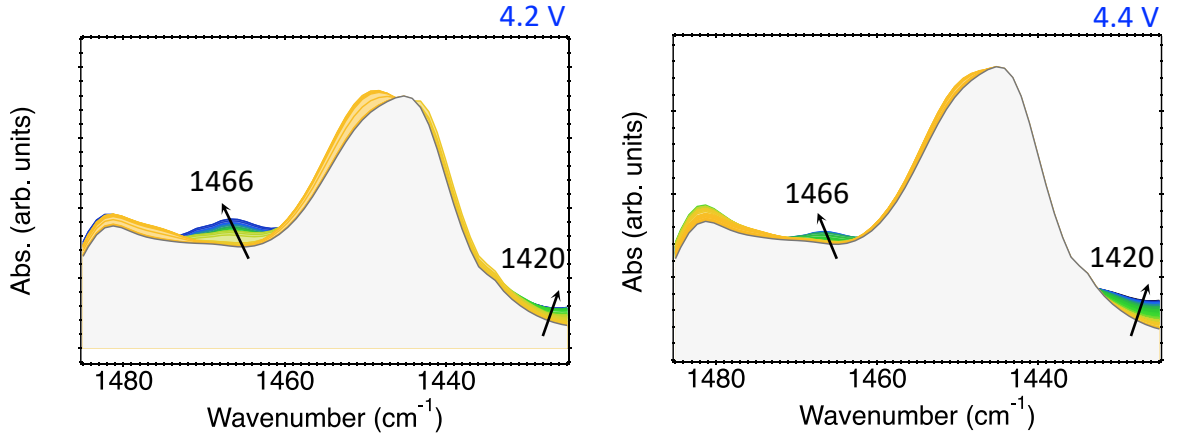
Transition Metal Redox Chemistry

- Reversible shift from 580 to 625 cm^{-1} of TM-O vibrational mode during cycling (on analyzing with XAS and XRD data).



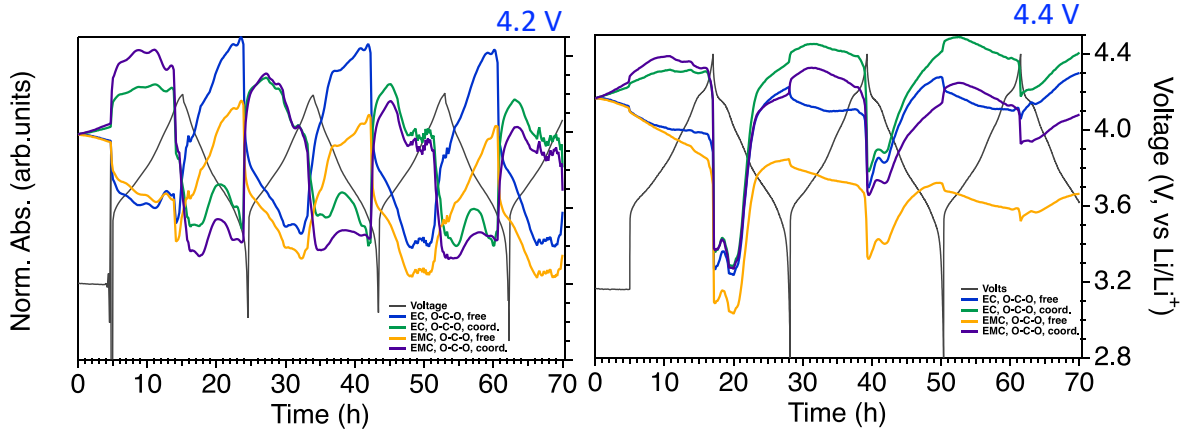
Cathode-Electrolyte Interphase Evolution

- New CEI species (e.g., carbonate) grow in at 1466 and 1420 cm^{-1} as cycling progresses.



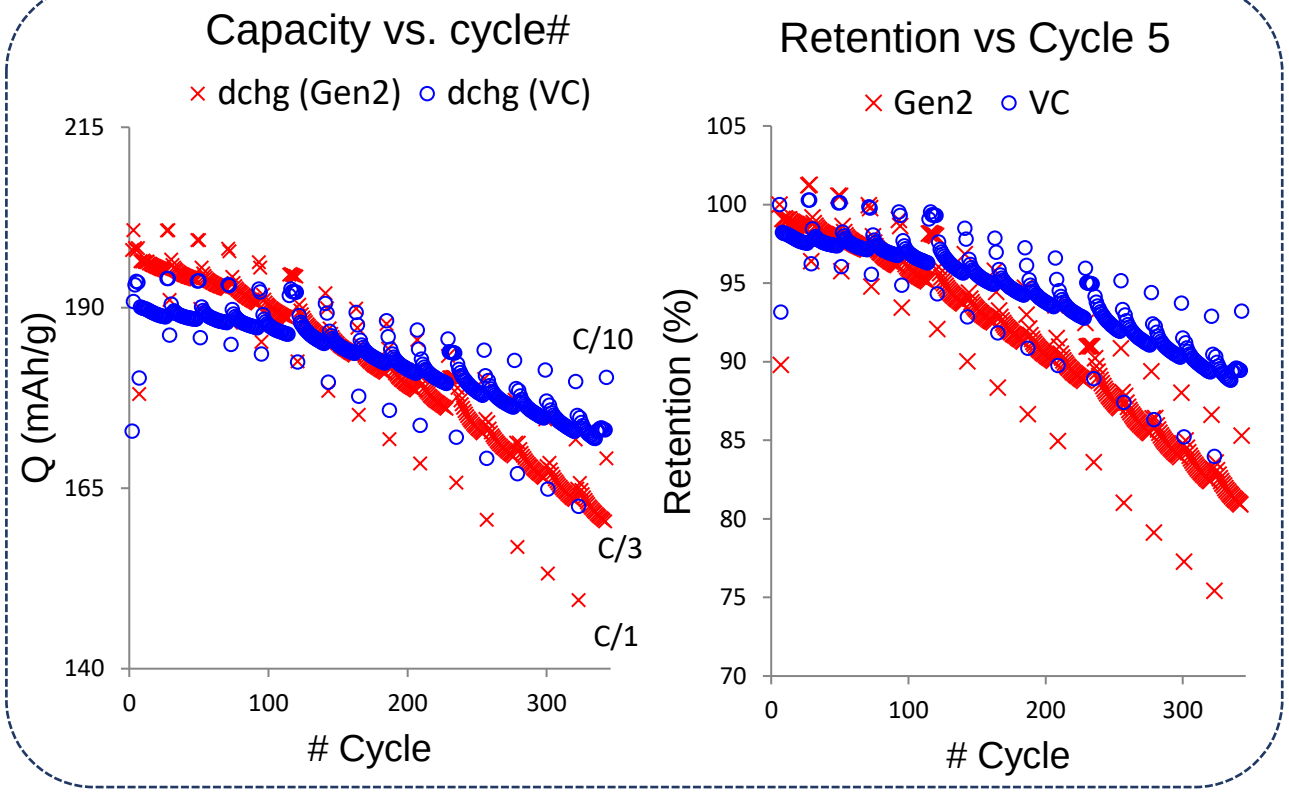
Electrolyte Solution Structure Changes

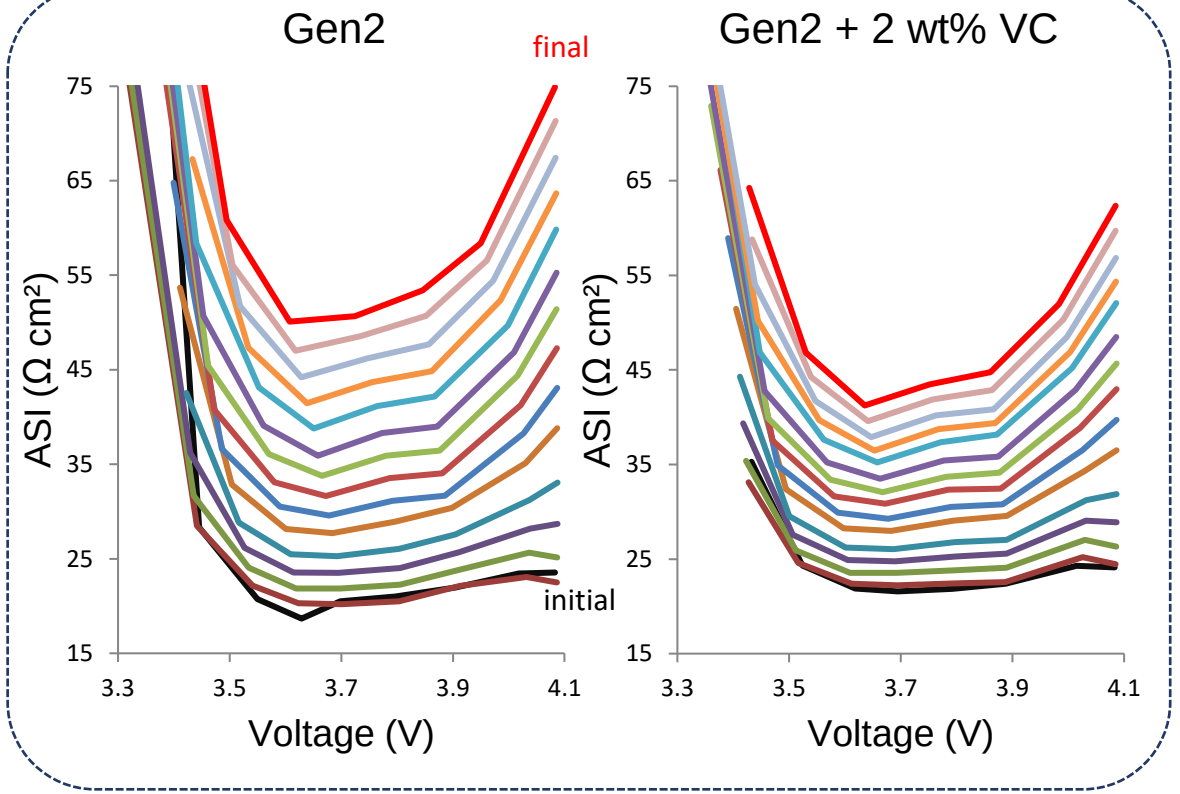
- Lattice parameter and unit cell volume changes based on different UCVs affect the electrolyte solution structure changes near the cathode surface.



$LiNi_{0.90}Mn_{0.05}Co_{0.05}O_2$//Gr cells display excellent performance

Additives, such as vinylene carbonate (VC) in Gen2 electrolyte, further improve performance

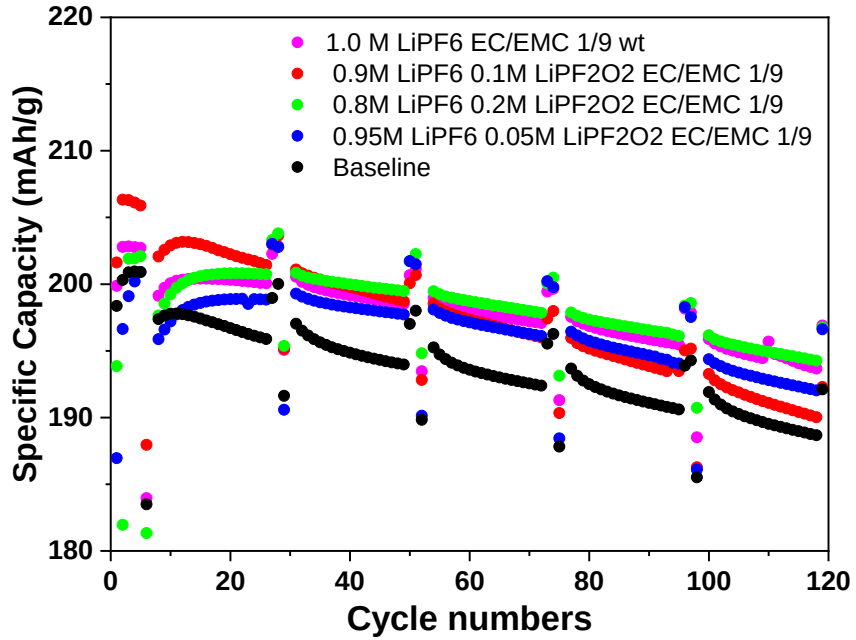




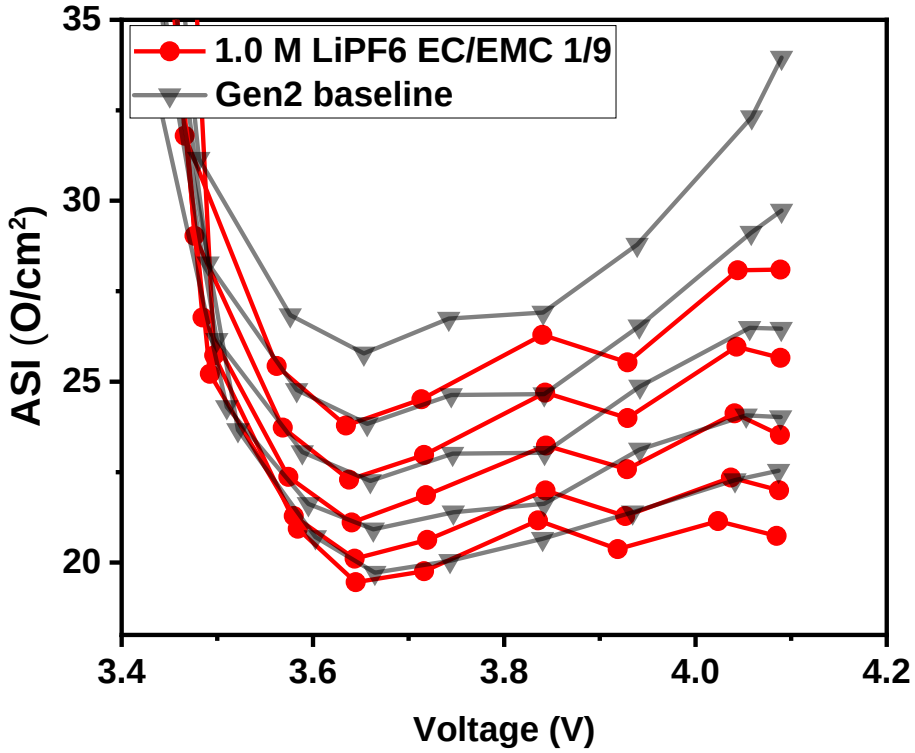
- Cells with Gen2 electrolyte have >85% capacity (@ C/10 rate) after ~360 cycles
- Initial capacity is lower and initial impedance is higher for cells with Gen2 + 2 wt% VC electrolyte.
- On long-term cycling, the VC cell displays better capacity retention and has lower ASI rise
- Data show importance of longer-term cycling for judging merits of electrolyte additives

Performance of $LiNi_{0.90}Mn_{0.05}Co_{0.05}O_2$//Gr cells in electrolyte with dual salt combinations and low (10%) ethylene carbonate

$LiPF_6$+$LiPF_2O_2$ (LiDFP) dissolved in EC:EMC (1:9 w/w) solvent: 3.0 – 4.2 V, 30 °C tests



Capacity fade for electrolytes with 1.0 M ($LiPF_6$ + LiDFP) or 1.0 M $LiPF_6$ in EC/EMC (1/9)



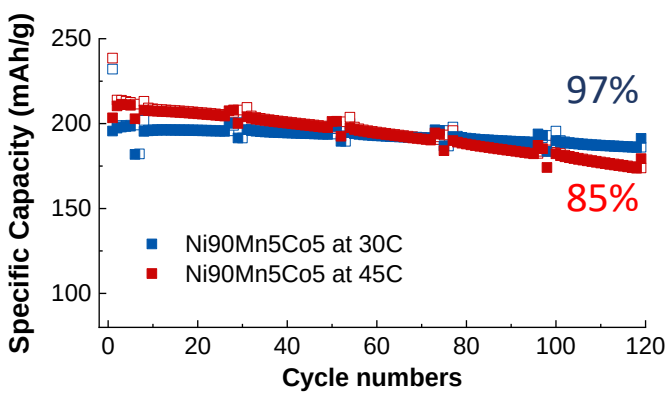
Impedance rise is slightly lower for the electrolyte with 1.0 M $LiPF_6$ in EC/EMC (1/9)

Electrolyte modifications can improve cell performance

Observations from $LiNi_{0.90}Mn_{0.05}Co_{0.05}O_2$ cycled in full cells

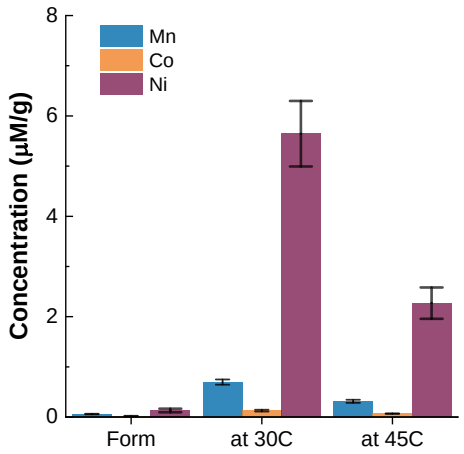
Diagnostic studies at the Argonne Post-Test Facility

Cycle retention of Ni90Mn5Co5//Gr cells (Gen2 electrolyte)

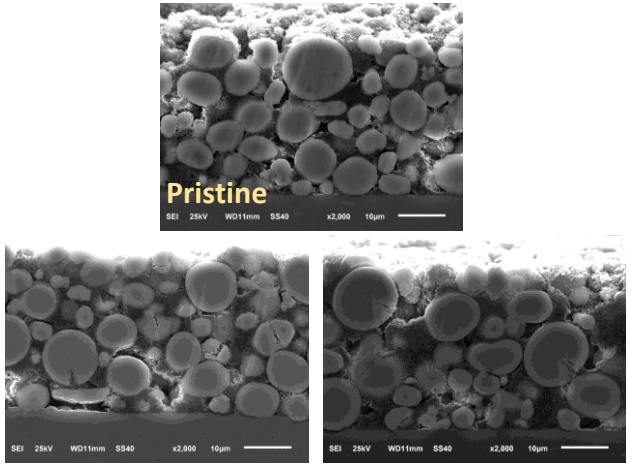


- Initial capacity and capacity fade are greater in cells cycled at 45°C than at 30°C
- Changes are observed in both the cathode and anode surface films in XPS data
- Transition metal (especially Ni) dissolve from the oxide
- No obvious differences in oxide cracking at 30 and 45°C

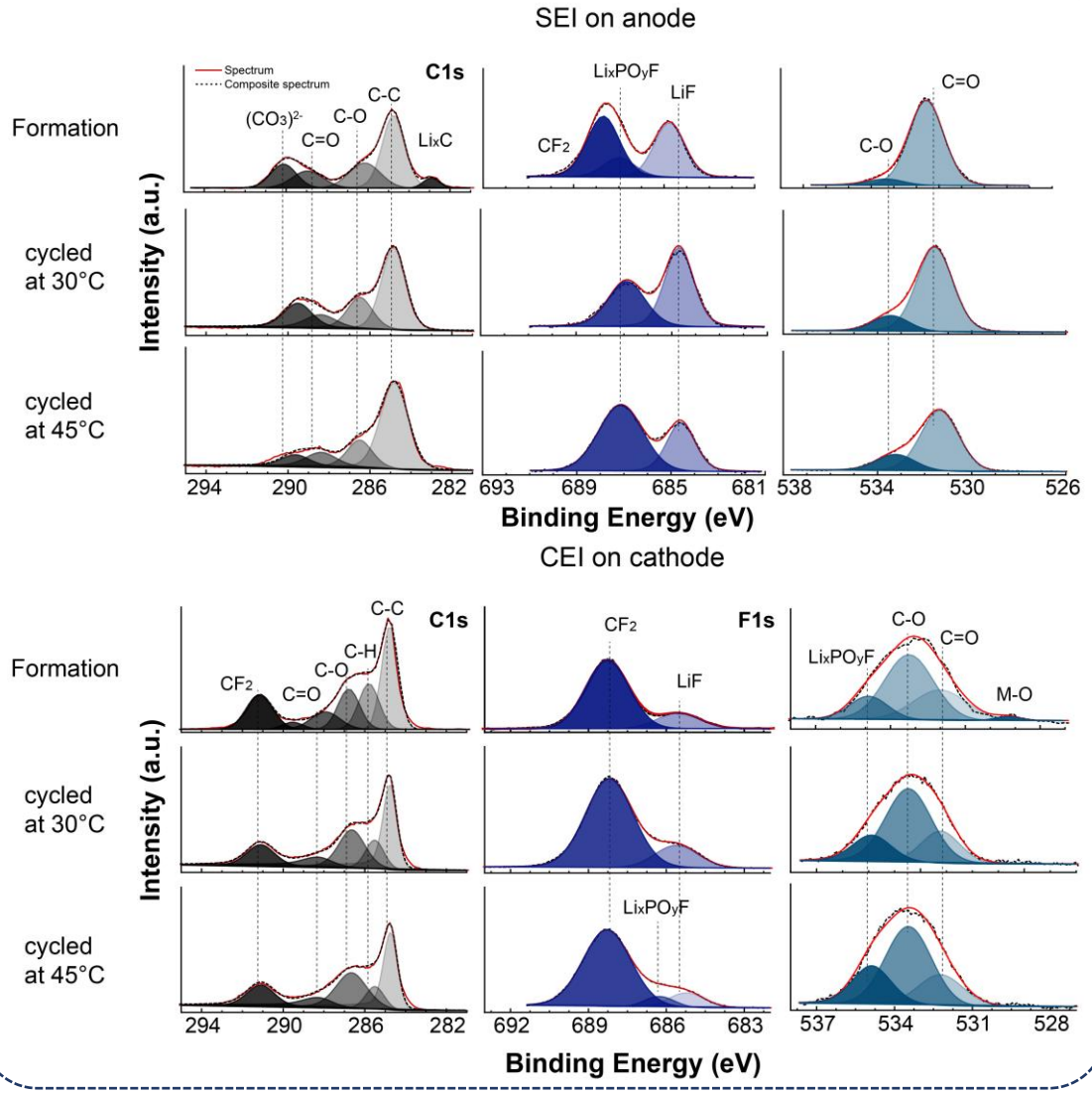
TM dissolution/deposition



Cross-section SEM



Interphase observation before and after cycling



TOF-SIMS analysis of pristine and cycled oxide electrodes

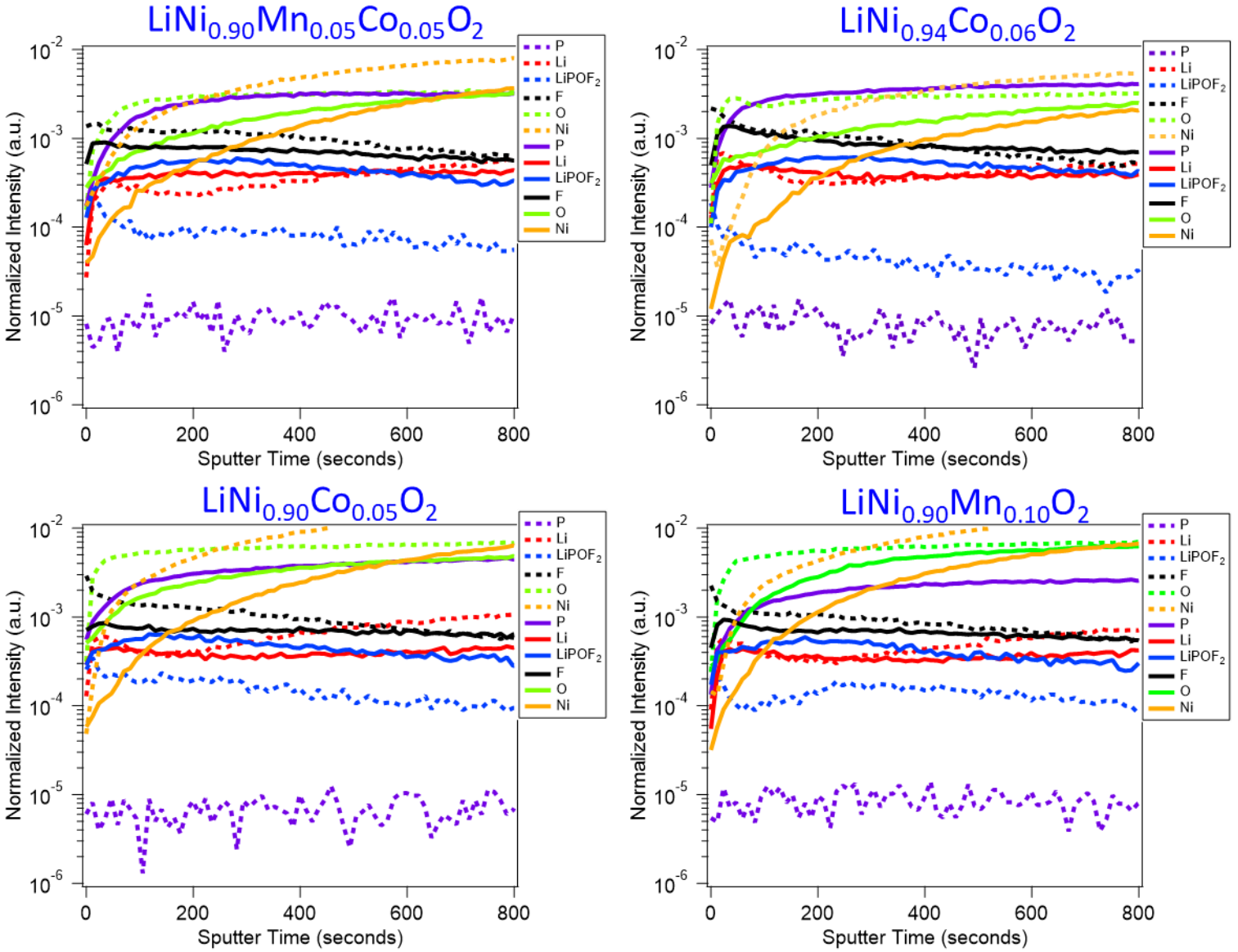
TOF SIMS test gives surface film composition and near-surface structure information.

Elemental composition of surface films

- Not much difference between the samples
  - Surface films are similar due to the same electrolyte (Gen2) used in all cells
  - Salt ($LiPF_6$) decomposition products (*e.g.*, $LiPOF_2$) are observed
  - Differences in electrochemical properties may be more related to differences in oxide bulk and surface structures.

Near Surface Structure of oxide

- Ni and O contents measured near the surface are lower in the cycled samples.
- Ni/O ratios are also lower after cycling.
  - Potential oxygen loss and Ni dissolution during cycling.



Dashed Lines = Pristine electrodes.
Solid lines = Cycled electrodes.

Response to Previous Year's Reviewer Comments

Query

For the DEMS tests, it would be worth knowing the reason to choose 4.2 V with prolonged holding to collect the O_2/carbon dioxide (CO_2) gassing data. In general, the preferred way to collect the gassing data would be during the galvanostatic charging at higher voltage, such as greater than 4.5 V.

Response

We have tested full cells at voltages > 4.2 V. In general, higher the cell voltage, greater the quantities of gas, which are generated because of electrolyte oxidation reactions at the positive electrode. Note that, unlike typical NMC oxides (e.g., $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$), $LiNiO_2$-based oxides do not deliver much higher capacities when full cell voltages exceed 4.2 V. In fact, crystal structural damage to the oxide is likely at higher voltages because of excessive delithiation. Hence, from these practical considerations, we limited most DEMS experiments to an upper voltage of 4.2 V.

Query

In the gassing behavior, it is not clear to the reviewer why other organic gases (other than O_2 and CO_2) are absent. Is it an experimental error? Gases containing hydrogen (H) and F atoms were expected.

Response

Indeed, other gases that arise during SEI formation on the graphite are present; they were just not reported in the slide.

Query

For DSC results, the onset temperature of the first exothermic peak should be discussed.

Response

The onset temperature in the DSC data were similar for all four oxide compounds shown in the slide.

Collaboration and Coordination

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Major Research Facilities

- Materials Engineering Research Facility
- Post-Test Facility
- Cell Analysis, Modeling, and Prototyping
- Spallation Neutron Source
- Environmental Molecular Sciences Laboratory
- Advanced Light Source
- Battery Manufacturing Facility
- Advanced Photon Source (APS)
- Laboratory Computing Resource Center (ANL)
- NMR Spectroscopy Lab (ANL)
- National Energy Research Scientific Computing Center (LBNL)
- Stanford Synchrotron Radiation Light Source

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Proposed Future Research

- Scale-up additional oxide compositions and evaluate using standard protocols
  - Examine compositions that have higher Mn content, such as derivatives of $LiNi_{0.5}Mn_{0.5}O_2$
- Develop oxide particle coatings and new electrolytes to mitigate performance loss
  - Identify coating techniques that can be easily scaled-up
  - Find electrolyte systems that show improved performance in thermal abuse tests
- Continue ongoing diagnostic tests and determine performance degradation mechanisms
  - Electrochemical (3-electrode cells, symmetric cells) and physicochemical (XRD, NMR, TEM/STEM, XAS, gas analysis, etc.) tests will continue to provide valuable information
  - Continue development of *in situ/operando* diagnostic techniques
- Establish electrochemical models to explain performance of low-Co oxide systems
  - Models are needed to explain changes in interfacial transport and kinetic parameters with SEI and surface modifications, explain parasitic currents during calendar-life holds, etc.

All future work is subject to change depending on funding levels

Summary

- Electrodes fabricated from Argonne-synthesized $LiNiO_2$ have been examined in full cells
  - Electrochemical tests show that the positive electrode is the sole contributor to cell impedance rise. The primary cause of cell capacity fade is Li^+ trapping in the graphite SEI. Oxide particle inactivation because of disordered regions (inferred from NMR and TEM data) created during the cycling is the secondary cause of capacity fade.
- Performance of $LiNi_{0.90}Mn_{0.05}Co_{0.05}O_2$//Gr cells is better than performance of $LiNi_{0.95}Mn_{0.05}O_2$//Gr, $LiNi_{0.95}Co_{0.05}O_2$//Gr and $LiNi_{0.9}Mn_{0.1}O_2$//Gr cells
  - The addition of Mn and Co lowers initial cell capacity but improves capacity retention. Initial capacity of $LiNi_{0.9}Mn_{0.1}O_2$//Gr cells can be increased by raising the cycling voltage limit from 4.2 V to 4.4 V; this, however, causes higher cell capacity fade and impedance rise.
- Lower gassing onset potentials and larger gas quantities are observed with increasing Ni-contents in the $LiNiO_2$ –based oxides.
  - $LiNiO_2$//Gr cells have a low gassing onset potential (4.1 V). Increasing test temperature can greatly lower gassing onset potentials and increase gas quantities.
- *In Situ* Spectroscopic Studies on $LiNi_{0.90}Mn_{0.05}Co_{0.05}O_2$//Li cells show Transition Metal redox changes, oxide-electrolyte interphase evolution and electrolyte structure modifications near the oxide surface
  - Changes are more prominent when the upper cycling limit is 4.4 V than at 4.2V
- Performance of $LiNi_{0.90}Mn_{0.05}Co_{0.05}O_2$//Gr cells can be improved by using appropriate electrolyte additives or by using new electrolyte systems
  - Addition to 2 wt% VC to the Gen2 electrolyte improves cell performance. Using dual salts ($LiPF_6$+$LiPF_2O_2$) also in Gen2 or low-EC solvents also show performance benefits.